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13. ABSTRACT (Maximum 200 Words) This research program entailed the investigation of the surface chemical and tribological (friction, lubrication, and wear) properties of titanium carbide (TiC), titanium nitride (TiN), and vanadium carbide (VC). These hard coating materials are potentially useful in enhancing the performance and extending the lifetime of lubricated spacecraft mechanisms. The program sought to establish the fundamental chemical and tribological properties of interfaces involving these materials and to understand the origin of differences between the materials, such that they may be specified and employed in DOD spacecraft mechanisms. The objective of the research was to establish a systematic understanding of the reactivity and friction of model metal carbide interfaces in terms of both the inherent properties of each material as well as the fundamental origin of differences between the materials. This objective was met by providing a base level of fundamental information regarding the chemical and tribological properties of these materials. It is envisioned that this information will allow the intelligent design of and selection of materials in future USAF satellite mechanisms.		
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Fundamental Investigations of the Surface Chemistry and Tribology of Metal Carbides and Metal Nitrides

Project period: 01/15/2000-11/30/2002

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2. Objectives:

This research program entailed the investigation of the surface chemical and tribological (friction, lubrication, and wear) properties of titanium carbide (TiC), titanium nitride (TiN), and vanadium carbide (VC). These hard coating materials are potentially useful in enhancing the performance and extending the lifetime of lubricated spacecraft mechanisms. The program sought to establish the fundamental chemical and tribological properties of interfaces involving these materials and to understand the origin of differences between the materials, such that they may be specified and employed in DOD spacecraft mechanisms.

The *objective* of the research was to establish a systematic understanding of the reactivity and friction of model metal carbide interfaces in terms of both the inherent properties of each material as well as the fundamental origin of differences between the materials. This objective was met by providing a base level of fundamental information regarding the chemical and tribological properties of these materials. It is envisioned that this information will allow the intelligent design of and selection of materials in future USAF satellite mechanisms.

The general methodology of the program involved the use of surface analytical instrumentation for the measurement of interfacial chemical reactivity of these materials with potential lubricant analogues. In addition, the fundamental friction and wear properties of the materials were investigated over a range of length scales. As the carbide and nitride materials are intended for use as hard coatings in lubricated environments, a significant effort was made to establish the base-level correlation between the chemical and tribological properties.

3. Description of Effort:

This report documents the cumulative results of the program investigating metal carbide and metal nitride materials. Efforts in this program have involved chemical and tribological investigations of a series of alcohol and ester species and have demonstrated activity of the metal carbides toward these adsorbates. In addition, efforts have involved chemical and tribological investigations of ester, phosphate, and fluorine containing adsorbates and have demonstrated significant activity of the metal carbides toward these adsorbates. Both favorable (formation of protective films) and deleterious (lubricant degradation) classes of reactivity were observed and continue to highlight the need for complete system design (substrate, coating, lubricant, environment) when implementing carbide materials. We have used density functional theory (DFT) cluster calculations as a means of evaluating the energetics and feasibility of different reaction pathways.

4. Accomplishments/New Findings

This research program entailed the investigation of metal carbides and nitrides as potential hard coatings for aerospace applications. In general, the program took the approach of correlating the surface chemical properties of these materials with fundamental measurements of their inherent tribological properties.

The following efforts were completed during the course of the program.

- Fundamental Surface Chemistry**

Investigations of the surface chemical properties of titanium carbide (TiC) and vanadium carbide (VC) were performed in a series of studies employing small molecular adsorbates. These studies have focused on developing a fundamental understanding of the reaction pathways exhibited by these complex compound materials. In the past, experiments have identified key differences in the reactivity of these two materials that relate to their specific electronic structure. In this grant year, the series of studies have continued in the form of temperature programmed desorption (TPD) measurements of ammonia adsorbed on TiC(100) and VC(100). While vibrational studies suggest similar bonding interactions with the two surfaces, TPD measurements indicate that some fraction of ammonia found in the first monolayers binds to VC to greater extent than on TiC. This result is currently being explored through ultraviolet photoelectron spectroscopy measurements designed to probe the molecular orbitals involved in the bonding interaction.

Detailed spectroscopic studies of the interaction of carbon monoxide (CO) with the (100) surfaces of titanium carbide (TiC) and vanadium carbide (VC) were performed for the first time and analyzed to provide insight into the nature of the surface chemical interactions. This work was pursued to develop a fundamental understanding of the surface bonding and reaction properties to enhance the use of TiC and VC as tribological materials and to gain insight into their potential use as catalysts. VC and TiC are both rocksalt materials but differ fundamentally in their electronic structure as the additional electron present in a formula unit of VC presents a significantly different surface bonding environment. CO has been used as a probe molecule to determine the relative electron accepting and donating tendencies of the substrates. Temperature-programmed desorption (TPD) has demonstrated that CO has a significantly higher heat of desorption on VC compared to TiC. High-resolution energy loss spectroscopy (HREELS) was used to measure surface vibrational frequencies, and the C-O stretch of reversibly adsorbed C-O is 2060 cm^{-1} on VC, and 2120 cm^{-1} on TiC, indicative of greater π -back-bonding on the VC surface. This enhanced back-bonding interaction is also observed in core level X-ray photoelectron spectroscopy satellite structure, and in valence band perturbations observed with ultraviolet photoelectron spectroscopy. Detailed analyses of these data show that CO has a slightly stronger σ -donor interaction with VC, but the stronger VC-CO bond is due primarily to the π -interaction that is essentially absent on the TiC surface. Density functional theory (DFT) has also been applied to small MC clusters that

qualitatively reproduce the observed experimental trends. DFT also provides compelling evidence of the impact of the electronic structure difference on the CO interaction, as occupied d-orbitals in VC participate in the back-bonding interaction, but these levels are unoccupied in TiC. The results are entirely consistent with a simplified molecular orbital description of the materials that results in the surface metal atoms of TiC behaving like d^0 species and those of VC as d^1 species. These formal occupations are greatly tempered by covalent mixing with carbon atoms in the lattice, but the electronic structure clearly plays a dominant role in the surface bonding of the carbides, controlling their reactivity with lubricants and reactants with which they come into contact.

The interaction of σ -donor adsorbate ammonia (NH_3) with $TiC(100)$ and $VC(100)$ surfaces has been investigated. Ammonia has been used as a probe for the surface reactivity over the range from 100 K to 400 K. Temperature programmed desorption (TPD) has been utilized to determine the desorption states of NH_3 . High-resolution electron energy loss spectroscopy (HREELS) probed the adsorption states and adsorption geometry of NH_3 on these substrates. Ultraviolet photoelectron spectroscopy (UPS) has been used to examine the valence electrons of NH_3 interacting with the surface. Ammonia showed a similar interaction with both TiC and VC. TPD displayed a desorption temperature for the monolayer feature that is the same for both substrates. HREELS spectra exhibited an identical blue shift of the umbrella mode on both surfaces as the temperature is increased. Finally, UPS showed the position of the $3a_1$ orbital is identical for NH_3 adsorbed on both TiC and VC. These experimental results were consistent with results obtained from density functional theory (DFT) calculations and were explained in terms of the similar σ -acceptor properties of the two substrates.

HREELS investigations of carbide surface chemistry were extended to the (111) face of the TiC crystal. This surface is technically relevant because it may dominate the surface of polycrystalline TiC coatings. Preliminary experiments with oxygen and carbon monoxide show that the (111) surface is more reactive than the (100) face, as predicted by the increased metallic character in the surface electronic structure. With oxygen exposure, we find evidence for oxygen adsorption at two different sites on the metal terminated surface: the titanium atop site ($Ti=O$, 1000 cm^{-1}) and a bridging site ($Ti-O-Ti$, 580 cm^{-1}). With increasing temperature, the adsorbed oxygen is driven to the more stable bridging site. Our analysis suggests that the surface is passivated by the oxidized titanium layer. VC (111) surfaces have also been prepared for similar study in the near future.

- **Alcohol Surface Chemistry.**

The reaction of methanol on the (100) surfaces of single crystal vanadium carbide (VC) and titanium carbide (TiC) has been studied using high resolution electron energy loss spectroscopy (HREELS), temperature programmed desorption (TPD), and x-ray photoelectron spectroscopy (XPS). Methanol forms a mixed monolayer of molecular methanol and a methoxy intermediate upon adsorption at 153K on both

VC(100) and TiC(100). With increasing temperature, methanol is evolved from both surfaces through molecular and recombinative desorption. Approximately half of the methoxy intermediate reacts with the VC surface to produce formaldehyde and hydrogen, with a small amount of methane and persistent oxygen surface species. By contrast, very little of the methoxy intermediate reacts with the TiC surface, producing methane and hydrogen. A model of the surface reactions has been constructed based upon differences in the electronic structures of the carbide substrates.

Studies of the surface chemistry of trifluoroethanol were initiated with TPD and HREELS. This work represents a natural extension of our previous work on small alcohol reactivity and has direct relevance to the use of perfluorinated lubricants with carbide coatings. For both TiC and VC, we find evidence for dissociative adsorption of trifluoroethanol through the alcohol functionality at cryogenic temperatures and subsequent reactivity at elevated temperatures. Albeit to a lesser extent than ethanol, trifluoroethanol reacts on VC to form a fluorinated alkene. On TiC, trifluoroethanol reacts through the cleavage of a C-C bond and appears to fragment the molecule. The origins of these reactive pathways remain under investigation, however the implications to the use of perfluorinated lubricants in systems containing metal carbide materials are immediately evident.

- **Ester Surface Chemistry.**

To model the reactivity of ester-based lubricants and additives with carbide surfaces, we have completed an investigation of methyl formate CH_3OCHO (MF) adsorption on VC and TiC(100). On both surfaces, variable coverages of MF were adsorbed at (or below) 150K and subsequently exposed to increasing temperatures up to 700K. The resulting adsorbed species were studied with HREELS and XPS, and desorbed species were studied with TPD. On TiC(100) at low temperature, we found a mixed monolayer of molecular (OCO mode at 1260 cm^{-1}) and dissociatively adsorbed MF. Products of dissociation are adsorbed methoxy (1050 cm^{-1}), formate (1320 cm^{-1}), and the oxametallocycle (1120 cm^{-1}) $\text{V}-\text{CH}_x-\text{O}-\text{V}$ species that was found after decomposition of small alcohols on VC. With increasing temperature, the TPD indicated molecular MF and methanol desorption at 270 K, corresponding to the loss of molecular MF and oxametallocycle peaks in the HREELS spectra. At 380 K, the methoxy evolved as methanol, leaving only formate up to 500K, and clean TiC at 700K. XPS results confirm these changes (retention of a carbon and oxygen containing species) and indicate a significant degree of surface oxidation in the temperature range 100-350 K. The results taken from the O 1s region also indicate a preferential reaction of the carbonyl oxygen at low temperatures.

On VC(100), we again found a mixed monolayer of molecular and dissociatively adsorbed MF, however the products of dissociation were methoxy (1050 cm^{-1}) and adsorbed CO (2050 cm^{-1}). At 170 K, molecular MF emission was observed with TPD, corresponding to the loss of molecular MF and CO peaks, in the HREELS. The reaction products from the remaining methoxy were similar to the products of

methanol decomposition on VC(100). That is, the oxametallocycle intermediate (1120 cm^{-1}) was formed from the methoxy at approximately 240K and given off at 470 K as methanol and formaldehyde. These results suggest a greater interaction of the carbonyl oxygen with TiC that produces the oxametallocycle and the formate species. The results of XPS measurements closely resemble those reported for the interaction of methyl formate on TiC.

- **Phosphate Surface Chemistry.**

The adsorption and reactivity of trimethyl phosphate ($(\text{CH}_3\text{O})_3\text{PO}$) (TMP), a simpler low molecular weight analogue of the lubricant additive tricresyl phosphate, has been studied on VC(100) using TPD, XPS, and HREELS. On TiC(100), adsorption and reactivity of TMP has been studied with HREELS. From the HREELS data at low temperature (110 K), major molecular peaks were observed on both substrates: P=O, P-(O-C), and (P-O)-C at ~ 1270 , ~ 1060 , and $\sim 860\text{ cm}^{-1}$ respectively. These peaks correlate well with those observed in the FTIR spectrum of neat TMP, suggestive of molecular adsorption on both substrates at this temperature. As the temperature is raised, the molecular phosphorus-oxygen vibrational features at 1270 and 860 cm^{-1} diminish on both surfaces. On TiC, a room temperature vibration from a reaction product (920 cm^{-1}) has been observed, along with apparent TiC oxidation ($\sim 570\text{ cm}^{-1}$) and other molecular fragments. At higher temperatures, two broad features remain on TiC at 795 and 1080 cm^{-1} , and a greater extent of surface oxidation is indicated. TPD and XPS studies will be performed to identify volatile reaction products and remaining surface species.

On VC, there is little molecular desorption indicated from TPD, strongly suggesting that the VC surface is active toward P-O bonds. Monolayer desorption data from VC indicate formaldehyde and methanol as primary products (similar to methanol/VC TPD). HREELS data at room temperature show changes related to the reaction of molecular TMP to strongly adsorbed fragments of the molecule. Some of these fragments persist in HREELS data after high temperature (700 K) anneals, potentially demonstrating evidence of altered methoxy chemistry on VC due to the influence of surface phosphorus species. A reaction product characterized by a 930 cm^{-1} on VC may be similar to that observed on TiC at low temperature. XPS revealed PO_x and residual carbon above 700 K, thus showing irreversible changes on the VC surface. Results to date indicate a relatively low energy pathway to decomposition, particularly on TiC, and strongly adherent reaction products. Work on this adsorbate will be concluded with TPD studies on the TiC (100) surface, and more detailed XPS work to examine the chemical state of the residual P and to examine the chemical change of the substrate indicated by the HREELS data on TiC.

The adsorption and reaction of triethyl phosphate ($(\text{CH}_3\text{CH}_2\text{O})_3\text{PO}$) (a relatively low molecular weight analogue of the lubricant additive tricresyl phosphate) has been studies on the VC(100) using TPD and X-ray photoelectron spectroscopy (XPS). These measurements indicate that both molecular and dissociative desorption profiles exist for this adsorbate. While the extent of reaction has not been quantified,

evidence is observed that C-O bond scission occurs with increasing surface temperature evolving CH_3CH_2^+ species. XPS measurements confirm that phosphorus and oxygen are retained on the VC surface following annealing treatments to 900 K.

- **Fluorine Related Chemistry.**

The interaction of fluorinated ethanol on titanium carbide (TiC) and vanadium carbide (VC) has been investigated by temperature programmed desorption(TPD), X-ray photoelectroscopy (XPS) and high resolution electron energy loss spectroscopy (HREELS). It was found that dissociation adsorption occurs for trifluoroethanol on both surfaces at cryogenic temperature, leading to the formation of a fluorinated ethoxy species. Fluorinated ethene is produced at elevated temperature. The reaction yield for defluorination of the alkoxy surface species is ~15% greater on VC (100) as compared to TiC(100). In addition, the adsorption and reaction of trifluoroethanol on oxidized and sputtered TiC and VC surfaces has been investigated in order to explore the influence of environmental aging of the carbide surfaces employed within lubricated contacts. It was found that oxygen pre-exposure enhanced dissociative adsorption of trifluoethanol, and blocked sites for molecular adsorption. Oxygen pre-exposure increases the production of fluorinated ethene to a limited extent. Likewise, the presence of surface defects, created through inert gas sputtering, is observed to increase the reactivity of carbide surfaces towards this fluorinated compound. While alcohol terminated perfloroethers such as ZDOL are not currently used within the satellite community, these results do portray a possible route for the design of boundary layer additives for use with perflorinated lubricants and metal carbide coatings.

- **Density Functional Theory (DFT) Modeling.**

Density Functional Theory (DFT) is widely used to describe the electronic structure of transition metals and their compounds. To augment our understanding of the effects of electronic structure on the surface chemistry and tribology of the transition metal carbides and nitride, we have applied DFT to calculations of the electronic structure of symmetric clusters to model the (100) surfaces that were the focus of our work in this program to date. In addition, we have generated clusters with small molecules (in particular, CO and NH_3) bonded to a metal atom in the same site symmetry as expected on the (100) surfaces to provide a theoretical estimate of the heat of adsorption, and to enable a comparison to our experimental electronic structure studies performed with UPS. To our knowledge, this work represents the first application of DFT to these materials. We have used commercially available software running on a desktop computer system.

We have found that the calculations accurately predict the adsorption energy of CO on TiC (100), and we calculate a significantly higher CO adsorption energy on VC, as we have observed experimentally. Furthermore, calculations on a TiN cluster show that it also adsorbs CO more strongly than does TiC, as was predicted for this material that is isoelectronic with VC. Importantly, we have not been able to perform

experiments on TiN as we lack a suitable single crystal surface – these theoretical results should provide useful information in lieu of such a sample. The electronic structures calculated were in good agreement with those measured experimentally with UPS, accurately predicting the energy splittings of the CO valence levels upon adsorption to TiC and VC. These results were described in some detail in the CO adsorption paper submitted to J. Phys. Chem. Furthermore, the calculations predict a very similar adsorption energy for NH₃ on both VC and TiC. Our experimental work on NH₃ adsorption has not yet concluded, but we have noted that similar desorption states exist on TiC and VC, although an additional species exists on VC that is more strongly adsorbed. In general, we are very pleased with the insights we have gained through these DFT calculations. They have verified the basic premise of this program and provide a potential pathway for understanding the interactions of more complex species on the surfaces of these materials.

The experimental study of more complex adsorbates on the metal carbide surfaces is starting to exceed our limited modeling capability using density functional theory (DFT). In the past year, we have completed work on adsorbates of increasing complexity, up to and including surface bound methoxy species using primarily 18 atom clusters (M₉C₉) for the (100) surface and 16 atom clusters (M₈C₈) for the (111) surface. Atoms and molecules studied include hydrogen, oxygen, fluorine, water, carbon monoxide, ammonia, methanol/methoxy. Pursuing further studies of larger molecules with potentially multiple sites for surface interaction requires the use of larger clusters to provide a sufficient number of chemically similar sites (requiring greater computational capability) or a more sophisticated modeling approach using periodic boundary conditions. To enable some understanding of the chemical nature of the trimethyl phosphate and methyl formate species described above, DFT calculations were performed on those molecules. The objective of such calculations is the evaluation of the electron donor/acceptor tendencies of the molecules such that we can relate their chemistry to smaller molecules that have already been studied.

Density Functional Theory (DFT) studies of M₈C₈ clusters to model the (111) surface were initiated. These calculations have predicted that the TiC (111) surface should exhibit a Ti 3d-based surface state, which has been observed experimentally. The calculations also predict that both TiC and VC (111) should have much stronger interactions with CO than has been observed and predicted for the (100) surfaces. The enhanced reactivity of both TiC and VC (111) surfaces is traceable to the added metal electron density caused by the presence of three dangling bonds, and in the case of CO adsorption, much stronger π -bonding interactions result.

DFT work on (100) surface defects has been pursued, looking at the impact of both oxygen substitution for carbon and the presence of carbon vacancies in the TiC lattice. The results of these studies were in keeping with our expectations based on the molecular orbital model. Specifically, substituting oxygen atoms for carbon adds two electrons to the cluster, and these electrons must occupy metal-based orbitals. We found that two oxygen atoms must be included in a Ti₉C₇O₂ cluster to impact the adsorption of CO by populating the appropriate π -bonding orbitals. This result

enables us to assess the effects of oxygen impurities in our single crystals and in real TiC materials, with an initial indication that impurity levels in excess of 20% should bring about measurable changes in surface chemistry. The presence of carbon vacancies had the anticipated effect of increasing metal electron density as well. Overall, these results show that the theoretical study of defects is a powerful method of understanding how these sites, which are difficult to study experimentally, impact surface chemistry.

According to our DFT results, the highest occupied molecular orbital of the TMP molecule is located primarily on the oxygen atom of the P=O group and has appropriate symmetry for σ -donor interactions with surface sites. The LUMO of this molecule is a π -orbital with significant density on this same atom, providing an additional driving force for bonding with sites having π -electron density, such as the V atom of VC. Relating to our experimental work, the molecular vibrational frequency perturbed at the lowest temperature is the P=O feature at 1270 cm^{-1} , supporting idea that the molecule initially bonds to the surface through that oxygen atom.

Methyl formate is the simplest ester molecule, and hence its interaction with surfaces will likely be less complex than larger esters. DFT reveals that the highest occupied orbitals have significant π -electron density on the carbonyl oxygen. Alternatively, the highest occupied orbital with symmetry appropriate for σ -donation is located on the alkyl (C-O-C) oxygen. The interactions of the ester with a surface may therefore depend on the availability of σ and π -acceptor sites, and hence one might predict a different interaction on TiC relative to VC and TiN. Experimentally, we see greater low temperature reactivity on TiC relative to VC, breaking the $\text{CH}_3\text{O-CHO}$ bond resulting in the formation of a surface methoxy group and a surface complex involving the carbonyl oxygen.

DFT studies were also initiated on TiN clusters to enable a comparison to the carbides that has been limited by the lack of experimental samples. Calculations on the Ti_9N_9 clusters have shown the expected similarity to the V_9C_9 populations of the metal valence levels based on their isoelectronic nature. In addition, the predicted adsorption energy of CO on the Ti_9N_9 (-21 kcal/mole) cluster is more similar to V_9C_9 (-25 kcal/mole) than to Ti_9C_9 (-13 kcal/mole), the result of π -bonding. Interestingly, the adsorption energy of NH_3 is predicted to be much greater on TiN than either of the carbides. We attribute the difference to a significantly greater positive charge on the Ti atom in the TiN cluster, creating a much stronger electrostatic interaction with the NH_3 dipole.

- **Microscopic Tribological Testing.**

Atomic-level tribological measurements have established that ethanol has a relatively low sticking coefficient at room temperature, and yet a carbonaceous film is observed to grow *across* the surface with increasing exposures. Specifically, XPS measurements have revealed that film growth initiates through a surface species

possessing an ~2:1 carbon to oxygen ratio, but continues beyond the first layer with a carbon rich composition. Surface topographs obtained with STM have clearly identified that film growth initiates at step edges of the single crystal substrate and continues to grow on to the terrace with increasing exposures. These STM measurements were instrumental in establishing that a friction reduction on the VC(100) surface is not realized until a complete monolayer is formed.

A study of the frictional properties of 1-octanol and 2,2,2-trifluoroethanol adsorbed on VC(100) at room temperature is presented. Atomic force microscopy (AFM) has been used to determine the changes in frictional response and interfacial adhesion. Scanning tunneling microscopy (STM) has been used to elucidate surface morphology. X-ray photoelectron spectroscopy (XPS) has been utilized to determine the composition of the species formed by the interaction of these adsorbates with the VC surface. Adsorption of 1-octanol on the VC(100) surface at room temperature causes a 16% reduction in the friction of clean VC. STM images, combined with XPS results, showed that 1-octanol does not completely cover the surface and that this coverage does not vary after a 500 L exposure. Adsorption of 2,2,2-trifluoroethanol on the VC(100) surface at room temperature produced an increase in friction while at the same time exhibiting a decrease in friction. This result is rationalized in terms of differences on the interfacial shear strength and compared to ethanol studies on the same surface.

- **Macroscopic Tribological Testing.**

One goal of this research program was to study the tribological properties of thin film carbide samples produced by viable deposition processes. To date, we have attempted to study the friction and lubrication of TiC films on steel flats produced by several different organizations with our ultrahigh vacuum tribometer. The results were very disappointing as the films, without exception, have delaminated relatively quickly when studied unlubricated under UHV conditions. We were able to measure friction for only a few revolutions due to severe wear of the TiC films. These results highlight the critical need for lubrication of these materials and show that the vacuum environment is particularly challenging for the carbide tribology. In addition, these measurements highlight the need for high adhesion between the substrate and the coating film. This obviously does not bode well for these materials for space applications, and further underscores the need for effective lubrication. Before delamination, friction coefficients of approximately 1.0 were found for a TiC film against a silicon nitride counterpart.

5. Personnel Supported During the Project

University of Houston

Rebecca Guenard, Graduate student.
Luis Fernandez Torres, Graduate student.

Celia Salmerón-Rodríguez, Graduate student.
Dr. Zhiying Chen, Postdoctoral fellow.
Dr. Scott S. Perry, Associate Professor.

The Aerospace Corporation

Dr. Stephen Didziulis, Staff scientist and tribology section manager.
Dr. Peter Frantz, Staff scientist.
Dr. Hyun Kim, Staff scientist.

6. Publications and Presentations

Papers published in refereed journals

The Frictional Properties of Titanium Carbide, Titanium Nitride, and Vanadium Carbide: Measurement of a Compositional Dependence with Atomic Force Microscopy, Seungwhan Lee, Oussama El-bjeirami, Scott S. Perry, Stephen V. Didziulis, Peter Frantz, and Gouri Radhakrishnan, *J. Vac. Sci. Tech.*, **18**(1) (2000) 69-75

The Coordination Chemistry of Transition Metal Carbide Surfaces: Detailed Spectroscopic and Theoretical Investigations of CO Adsorption on TiC and VC (100) Surfaces, Stephen V. Didziulis, Peter Frantz, Luis Fernandez Torres, Rebecca Guenard, Oussama El-Bjerami, and Scott S. Perry, *J. Phys. Chem. B*, **2001**, *22*, 5196.

Chemical Modification of the Interfacial Frictional Properties of Vanadium Carbide Through Ethanol Adsorption B. I. Kim, S. Lee, R. Guenard, L.C. Fernandez Torres, and S. S. Perry, Peter Frantz and Stephen V. Didziulis, *Surf. Sci.* **2001**, *1-3*, 185.

Progress in the Pursuit of the Fundamentals of Tribology, Scott S. Perry, *Tribology Letters*, **2001**, *10*, 1.

L. C. Fernández-Torres, S. S. Perry, S. V. Didziulis and P. P. Frantz, "The Interaction of Ammonia with Transition Metal Carbide Surfaces," *Surf. Sci.* **2002**, *511*, 121.

P. Frantz, S. V. Didziulis, L. C. Fernandez-Torres, R. L. Guenard, and Scott S. Perry "The Reaction of Methanol with TiC and VC (100) surfaces," *J. Phys. Chem. B* **2002**, *106*, 6456.

R. L. Guenard, L. C. Fernandez-Torres, B.I. Kim, S. S. Perry, P. Frantz, and S. V. Didziulis, "Selective Surface Reactions of Single Crystal Metal Carbides: Alkene Production from Short Chain Alcohols on Titanium Carbide and Vanadium Carbide," *Surf. Sci.* **2002**, *515*, 103.

7. Interactions/Transitions

Presentations - Invited

Stephen V. Didziulis, Peter Frantz, P. Ann Bertrand, and Scott S. Perry "Fundamental Approaches to Spacecraft Tribology Issues" American Physical Society Meeting in Minneapolis, MN, March 22, 2000.

Didziulis, S. V.; Frantz, P.; Fernandez, L.; Guenard, R.; El-Bjeirami, O.; Perry, S. S. "Experimental and Theoretical Probes of Metal Carbide Surface Bonding," 2000 International Chemical congress of Pacific Basin Societies, Honolulu, HI, 19 December 2000.

Perry, S. S.; Guenard, R.; Fernandez, L.; El-Bjeirami, O.; Frantz, P.; Didziulis, S. V. "Surface Chemical Reactivity of Single Crystal Metal Carbides," 2000 International Chemical congress of Pacific Basin Societies, Honolulu, HI, 19 December 2000.

Perry, S. S. "Chemical and Materials Properties of Metal Carbide Surfaces", Department of Chemistry, Vanderbilt University, February 20, 2001.

Perry, S. S., Kim, B.I., Guenard, R. L., Didziulis, S.V.; Frantz P.; Fernandez-Torres, L.C.; "Surface Chemical Reactivity of Single Crystal Metal Carbides" American Chemical Society National Meeting, San Diego, CA, 2 April 2001.

Perry, S. S., Kim, B.I., Guenard, R. L., Didziulis, S.V.; Frantz P.; Fernandez-Torres, L.C.; "Chemical Modification of the Interfacial Frictional Properties of Vандium Carbide Through the Adsorption of Small Molecules" Colloids and Surface Chemistry Meeting, American Chemical Society, Pittsburgh, PA, June 11, 2001.

Scott S. Perry "Correlation of Tribological and Surface Chemical Properties of Metal Carbides", CSEM, Neufchatel, Switzerland, October 2001

Scott S. Perry, "Atomic Scale Tribochimistry", Tribology Gordon Conference, Roger Williams University, Bristol, RI, August 2002

Presentations- Contributed

Luis Fernandez Torres, Rebecca Guenard, Oussama El-Bjerami, Stephen V. Didziulis, Peter Frantz, and Scott S. Perry, "Substrate Dependent Interactions of Carbon Monoxide and Ammonia on Metal Carbide Surfaces", Texas Surface Science Round-Up, Round Top, TX, May 26, 2000

Rebecca Guenard, Luis Fernandez Torres, Stephen V. Didziulis, Peter Frantz, and Scott S. Perry, "Selective Surface Reactions of Single Crystal metal Carbides: Alkene Production from Ethanol on Titanium Carbide and Vanadium Carbide", Texas Surface Science Round-Up, Round Top, TX, May 26, 2000

B.I. Kim, Seunghan Lee, Rebecca Guenard, Luic Fernandez Torres, and Scott S. Perry, "Chemical Modification of the Interfacial Frictional Properties of Vanadium Carbide Through Ethanol Adsorption",

Texas Surface Science Round-Up, Round Top, TX, May 26, 2000

Didziulis, S.V.; Frantz P.; Fernandez-Torres, L.C.; Perry, S. S. "Metal Carbide Electronic Structure Effects on Surface Chemistry and Tribology" American Chemical Society National Meeting, San Diego, CA, 2 April 2001.

Perry, S. S., Kim, B.I., Guenard, R. L., Didziulis, S.V.; Frantz P.; Fernandez-Torres, L.C.; "Chemical Modification of the Interfacial Frictional Properties of Vandium Carbide Through the Adsorption of Small Molecules" American Chemical Society National Meeting, San Diego, CA, 2 April 2001.

Stephen V. Didziulis, Peter Frantz, Luis C. Fernández-Torres, Rebecca L. Guenard, Oussama El-Bjeirami, and Scott S. Perry, "Substrate-Dependent Interaction of Carbon Monoxide and Ammonia on Metal Carbide Surfaces"; poster presented at the American Vacuum Society 47th International Symposium, Boston, MA October 4, 2000.

Rebecca L. Guenard, Luis C. Fernández-Torres, Scott S. Perry, Peter Frantz, and Stephen V. Didziulis Selective, "Surface Reactions of Single Crystal Metal Carbides: Alkene Production from Short Chain Alcohols on Titanium and Vanadium Carbide", American Vacuum Society 47th International Meeting, Boston, MA, Oct 2-6, 2000.

Perry, S. S. "Adsorption, Growth, and Characterization of Organic Thin Films", LSST Group Meeting, Lugano, Switzerland, August 28, 2001.

Interactions

The use of hard-coated components in spacecraft mechanisms is accelerating, typically with a steel counterpart. Specific examples include the use of TiC-coated balls in NASA Chandra and EOS reaction wheels, in GOES and POESS filter wheels, and their potential use in USAF programs currently in the design phase. This year, S. V. Didziulis participated in a readiness review of the POESS/TIROS instruments employing bearings with TiC-coated balls, including briefings to NOAA and NASA. In addition, S. S. Perry interacted with members of the technical staff of CSEM (Neufchatel, Switzerland) with regard to the future design of carbide coatings for bearing systems. In general, little attention is paid to the lubricants used based on the general belief that the pairing of unlike materials (carbide against steel) will prolong the life of the lubricants involved. This program is progressing in a manner that will enable the selection of appropriate lubricants and additives based on fundamental scientific principles rather than trial and error. Once the fundamentals have been established, Aerospace will be able to transmit the information directly to contractors involved in the manufacture of space hardware, leading to improved performance of Air Force, DoD, and NASA space systems.

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8. New discoveries, inventions, or patent disclosures.

9. Honors/Awards:

Prof. Scott S. Perry
Tenure and Promotion to Associate Professor
September 2000

Prof. Scott S. Perry
Appointment to Editorial Board of *Tribology Letters*
August 2001

Prof. Scott S. Perry
University of Houston Award for Research Excellence and Scholarship
Associate Professor Level
April 2002

Dr. Rebecca Guenard
Ph.D. in Chemistry awarded July 2002.
"The Reactivity of Molecules Containing Lubricant and Additive Functional Groups on
Vanadium Carbide and Titanium Carbide"